Pulsed laser deposition of Cu:Al_2O_3 nanocrystal thin films with high third-order optical susceptibility

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Nanocomposite films comprising metal Cu nanocrystals embedded in an Al_2O_3 matrix were deposited by alternating pulsed laser ablation from metallic Cu and ceramic Al_2O_3 targets. The films were grown in vacuum on glass substrates held at room temperature. The as-grown films contain 4 nm Cu nanocrystals in an amorphous Al_2O_3 matrix, with a total thickness of 190 nm. The films show a substantial third-order susceptibility with an electronic nonlinear refractive index of $(2.93 \pm 1.08)\cdot 10^{-10}$ cm^2 W^{-1} and a nonlinear saturation of $-(2.34 \pm 0.18)\cdot 10^{-5}$ cm W^{-1}. © *1997 American Institute of Physics.* [S0003-6951(97)03743-1]

Composite materials comprising metallic nanocrystals embedded in dielectric matrices exhibit interesting properties that can be engineered with the proper choice of metal and matrix. Such composites have been synthesized by quenching and heat treatments,[1] sol-gel processes,[2] sputtering co-deposition,[3] and ion implantation.[4] Most of these techniques are multi-step processes, in which a post-deposition treatment is often needed to optimize the properties. However, these treatments can also alter the average size, size distribution, and spatial arrangement of the nanoclusters,[5,6] with possible unfavorable effects particularly on the linear and nonlinear optical properties of the nanocomposite.

Unlike these methods, multiple-target sequential pulsed laser deposition (PLD), permits independent control of synthesis of the nanocrystals and the embedding matrix.[7] PLD has shown particular success in stoichiometric thin film deposition of complex oxides. Energetic (>100 eV) ions produced by ablation yield smooth, high-density films with good adhesion, especially desirable properties for optical applications.[8] Indeed, several optical applications—including second-harmonic generation[9] and light emission at 1.54 μm in planar waveguides[10]—have been demonstrated in films grown by PLD.

In this letter we report the fabrication by alternating-target PLD of Cu nanocrystals embedded in an Al_2O_3 matrix. The nanocomposite exhibits a large nonlinear index of refraction with significantly reduced saturable absorption compared to Cu:SiO_2 nanocomposites prepared by ion implantation. The Cu:Al_2O_3 system was chosen since the linear and nonlinear optical properties of Cu nanocrystals produced by other techniques have been widely studied.[11,12] In addition, Al_2O_3 has a high transparency and high refractive index, and optically doped Al_2O_3 films with good properties have been previously grown by PLD.[10]

The films were deposited using an ArF excimer laser [193 nm, 12 ns full width at half maximum (FWHM), 5 Hz repetition rate] focused alternately onto high-purity targets of Al_2O_3 ceramic or metallic Cu, at a typical fluence of about 2 J cm^{-2}. The targets were mounted in a computer-controlled holder 32 mm from the substrate, and rotated during ablation to prevent crater formation. The films were all grown in vacuum (10^{-7} Torr) and the substrates were held at room temperature. The film thickness and deposition rate were monitored continuously by tracking the reflection coefficient of a He–Ne laser during PLD,[13] calibrated by *in situ* reflectivity curves from pure Al_2O_3 and Cu films.

The nanostructure of the films was analyzed by high resolution (HR) transmission electron microscopy (TEM) of a sandwich structure of Al_2O_3/Cu/Al_2O_3 deposited by PLD on carbon-coated mica substrates. The deposition sequence was 1500 pulses on the Al_2O_3 target, then 160 pulses on the Cu target, followed by deposition of a top layer of Al_2O_3 to prevent oxidation of the Cu nanoparticles. This configuration was chosen so that Cu nanocrystals from different layers did not overlap in the HRTEM images. HRTEM specimens were prepared by floating the films off the mica substrate in deionized water, then picking them up on a copper grid. They were analyzed in plan view using a JEOL 4000 EX transmission electron microscope operated at 400 kV (point-to-point resolution 0.16 nm). Figure 1(a) shows that the film exhibits a very homogeneous distribution of dark areas on a homogeneous background. In the HRTEM image [Fig. 1(b)], crystal lattice fringes from the Cu nanocrystals can be seen in the dark areas. The lack of order in the background contrast shows that the embedding Al_2O_3 matrix is amorphous. From Fig. 1(b) we measured an average diameter of 3 ± 1 nm for the Cu clusters, with an average crystallite separation of 8 ± 1 nm, that is, twice the cluster diameter, which means that the nanoparticles are well isolated from each other. The density of crystallites in the film measured from the HRTEM images is $2.1\cdot 10^{12}$ cm^{-2}. Figure 1 clearly shows that PLD in vacuum produces a more homogeneous spatial distribution of nanocrystallites with narrower size distribution than either sol-gel synthesis[2] or ion implantation.[14]

For optical characterization, Cu:Al_2O_3 thin films were

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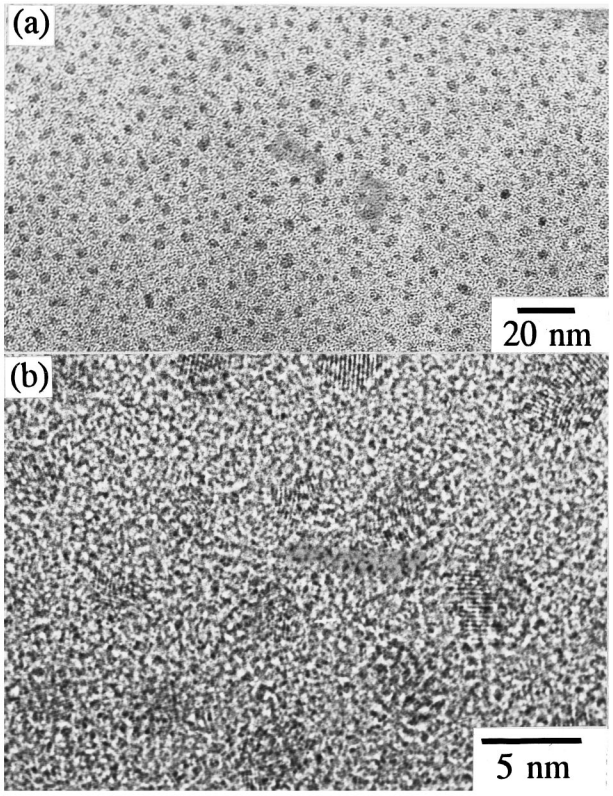

FIG. 1. TEM images of PLD Al_2O_3/Cu/Al_2O_3 film. (b) is a HRTEM image, showing the presence of the interference fringes in the Cu clusters (dark areas).

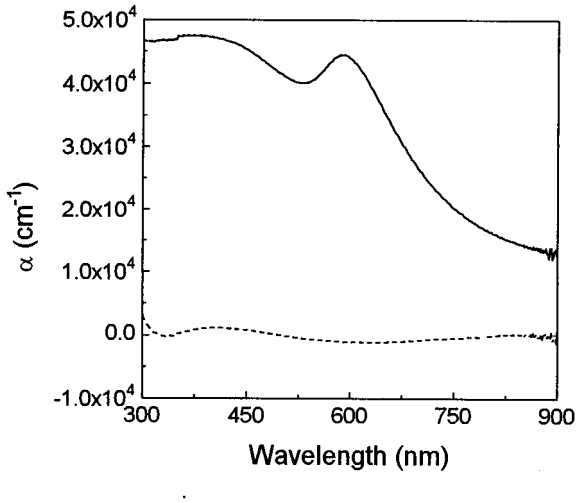

FIG. 2. Linear absorption coefficient (α) as a function of wavelength for the Cu:Al_2O_3—and the Al_2O_3 (--) film. Notice the appearance of the surface plasmon resonance peak at $\approx$590 nm when Cu nanoparticles are introduced in the Al_2O_3 matrix.

grown under the same deposition conditions, but the Al_2O_3/Cu alternating structure was repeated up to 10 times, producing films 190 ± 10 nm thick. The total Cu areal density was calculated from reflectivity curves to be 1.3×10^{17} atoms/cm^2, comparable to Cu:SiO_2 nanocomposites produced by ion implantation.[15] The films were deposited on 0.1-mm-thick Corning glass substrates to minimize the substrate contribution to the optical measurements. An Al_2O_3 reference sample with no Cu content was also grown.

Figure 2 shows that the absorption of the Al_2O_3 reference film is negligible in the visible, showing its good optical quality. However, when Cu nanocrystals are present in the amorphous Al_2O_3 matrix, the spectrum shows substantial absorption peaked around 590 ± 5 nm, due to the surface plasmon resonance (SPR) of Cu nanoparticles.[14] The linear absorption coefficient of the film at the peak of the SPR is $\alpha_0=(40\pm4)\cdot10^3$ cm^{-1}.

The nonlinear absorption coefficient (β) and the nonlinear refractive index of the films were determined by z-scan.[16] The beam from a cavity-dumped, synchronously pumped, mode-locked dye laser tuned to 596 nm (pulse duration 6 ps, repetition rate 3.8 MHz) was focused by a 150 mm lens to a waist of 35 μm, giving a maximum irradiance of $4\cdot10^7$ W cm^{-2}. The Rayleigh range z_0 of the beam was 6.2 mm, much longer than the thickness of either substrate or film. The on-axis transmission of the sample was measured by a small-aperture (SA) photodiode detector 90 cm from the lens; 8% of the total transmitted beam was split off just after the sample and monitored by an open-aperture (OA) detector. Both the SA and OA signals were normalized to incident laser power. The SA detector is sensitive both to nonlinear refraction and nonlinear absorption, the OA detector only to the latter. Each z-scan spectrum is a sequence of 700 points taken over the 40 mm interval in approximately 90 s; at each point, the photodiode signal is sampled 255 times, averaged and normalized to yield values for the OA and SA readings.

Figure 3 shows the variation of the OA and SA detector signals as a function of sample position (z). The shape of the SA z-scan indicates a positive value for n_2, while the OA z-scan exhibits weak nonlinear saturation. The solid lines in Fig. 3 are the error-weighted, best chi-square fits to the data using a fitting function of the same form as Eq. (A4) of Ref. 16. The nonlinear phase shift incorporates both thermal and electronic contributions to the nonlinear refraction which are separable by their differing z-dependences:[15]

$$\Delta\Phi_{\mathrm{el}}=\frac{kL\cdot n_2 I_o}{\left(1+z^2/z_o^2\right)^2}, \tag{1a}$$

$$\Delta\Phi_{\mathrm{th}}=kL\cdot\frac{dn}{dT}\Delta T=kL\cdot\frac{dn}{dT}\cdot\frac{P\alpha_0}{\kappa}\cdot\frac{1}{\left(1+z^2/z_0^2\right)}. \tag{1b}$$

Here k is the wave number, L the sample thickness, T the temperature, and κ the thermal conductivity. The nonlinear saturation (β), and the thermal ($n_{2\mathrm{th}}$) and electronic (n_{2e}) components of the nonlinear refractive index (n_2), were obtained from a global fit to OA and SA detector data from five different z-scan data scans taken at maximum intensities from $2.1\cdot10^7$ to $3.9\cdot10^7$ W cm^{-2}. The experimental values were $\beta=-(2.34\pm0.18)\cdot10^{-5}$ cm W^{-1}, $n_{2e}=(2.93\pm1.08)\cdot10^{-10}$ cm^2 W^{-1}, and $n_{2\mathrm{th}}=(1.24\pm0.18)\cdot10^{-9}$ cm^2 W^{-1}. z-scans of the Al_2O_3 reference film were flat, confirming that the Cu nanocrystals give rise to nonlinearity.

Near the SPR, n_{2e} is dominated by transitions from the d band to quantum-confined electrons in the s-p conduction band.[17] Pump-probe[12] and four-wave mixing[18] experiments show that interband excitation of Cu:SiO_2 composites near the SPR is relaxed by fast electronic collisions within the nanocrystal on a scale of 1–4 ps, and by slower electron–

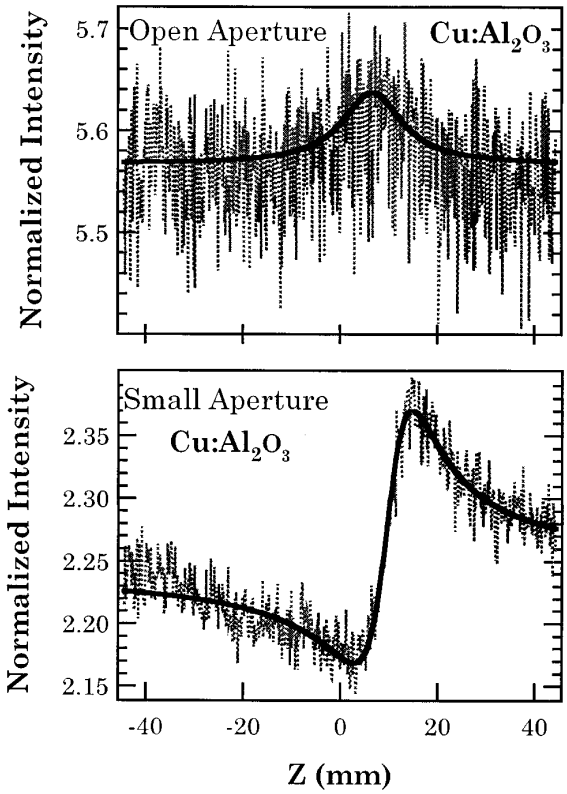

FIG. 3. Simultaneous open-aperture (OA) and small-aperture (SA) z-scans from the $Cu:Al_2O_3$ film at a maximum intensity of $3.7\cdot 10^7$ W cm^{-2}. The fainter dashed lines are the experimental data. The solid curves are the best-fit to the data.

phonon coupling to the matrix[19] ($\sim 50-200$ ps). Both processes are fluence- and size-dependent; in our experiment, relaxation times should be at the small end of the stated ranges. The real part of the electronic third-order susceptibility $\chi^{(3)}$ is $\mathrm{Re}|\chi^{(3)}|\approx(2.06\pm 0.77)\cdot 10^{-8}$ esu, within a factor of 2 of the value of $|\chi^{(3)}|$ for $Cu:SiO_2$ off the SPR measured by a technique sensitive only to the electronic component of $\chi^{(3)}$.[18]

Compared to the nonlinear optical properties reported for $Cu:SiO_2$ samples made by ion implantation,[14] the nonlinear saturation in the PLD-grown material is two orders of magnitude smaller, whereas the nonlinear refractive index is of comparable magnitude; measurable nonlinear effects occur at an intensity almost an order of magnitude smaller. These differences may be attributed to the fact that PLD yields nanoparticles that are more homogeneous in diameter and in distribution than those obtained by other techniques, since both cluster distribution and shape influence the linear and nonlinear optical properties of the nanocomposite.[20]

In summary, we have demonstrated that PLD in vacuum produces composites in which Cu nanocrystals with a remarkably homogeneous spatial and size distributions are embedded in Al_2O_3. The nonlinear refractive index for the $Cu:Al_2O_3$ films made by PLD is as large as that obtained for films made by other techniques, while the nonlinear saturation parameter is two orders of magnitude lower. The results thus show the excellent potential of PLD for producing nanocrystal-composite thin films in a single-step fabrication process, requiring no post-deposition treatments to optimize the optical or structural properties of the samples.

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